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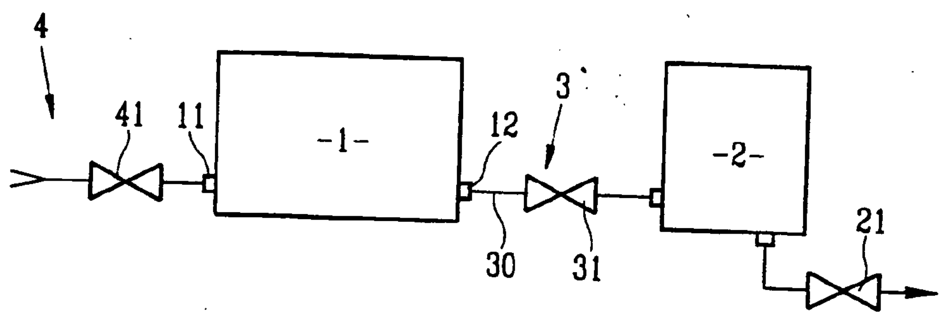
(54) **PROCESSUS DE PURGE DU CIRCUIT DE GAZ D'UNE PILE A COMBUSTIBLE, ET APPAREIL POUR LA MISE EN OEUVRE DE CE PROCESSUS**

(54) **PROCESS FOR FLUSHING THE GAS CIRCUIT OF A FUEL CELL, AND APPARATUS FOR PRACTICING THE PROCESS**



(57) The present invention relates to a process for purging the gas circuits of fuel cells, adapted to evacuate from these circuits, the water in liquid phase which may be there, as well as if desired the unusable gases or the like that the circuit is adapted to channel, for example nitrogen in circuits adapted for the circulation of hydrogen of air-hydrogen cells; it also relates to a device for practicing this process.

ABSTRACT OF THE INVENTION

The present invention relates to a process for purging the gas circuits of fuel cells, adapted to evacuate from these circuits, the water in liquid phase which may be there, as well as if desired the unusable gases or the like that the circuit is adapted to channel, for example nitrogen in circuits adapted for the circulation of hydrogen of air-hydrogen cells; it also relates to a device for practicing this process.

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PROCESS FOR FLUSHING THE GAS CIRCUIT OF A FUEL CELL, AND APPARATUS FOR PRACTICING THE PROCESS

The invention relates to a process for purging the gas circuits of fuel cells, adapted to evacuate from these circuits, the water in liquid phase which may be there, as well as if desired the unusable gases or the like that the circuit is adapted to channel, for example nitrogen in circuits adapted for the circulation of hydrogen of air-hydrogen cells; it also relates to a device for practicing this process.

In fuel cells at the anode of which hydrogen is consumed, a portion of the water produced on the cathode side of the cell passes through the membrane and accumulates in the compartment for hydrogen. So as to get rid of this water, it is necessary to carry out regularly purges of the hydrogen circuit. The frequency of the necessary purges largely depends on the cell, and is of the order of several seconds to several minutes. In the absence of purging, there will be seen a progressive degradation of the performance of the cell. Purges permit returning approximately to the initial performance; they moreover permit eliminating nitrogen which concentrates in the hydrogen compartment by diffusing through the membrane, as well as possible impurities present in the hydrogen.

At present, purging the hydrogen circuit of fuel cells is carried out toward the outside, and there results a loss of hydrogen; to limit this loss, it is the practice to limit the flow rate at the outlet of the cell; however, it is not necessary to greatly delimit this flow, because the purges lose their effectiveness if the hydrogen flow at the outlet is insufficient; a total hydrogen loss being unable to be reduced below several percent, this correspondingly decreases the yield of combustible. It has been proposed to operate the cell in a "closed circuit", and to re-inject the hydrogen at the input of the latter with the air of a circulator; it is thus possible to cause the cell to operate with purges that are much greater spaced, serving to eliminate the nitrogen from the cathode portion in the case of cells in which the combustible is oxygen supplied by a circulation of air; another advantage of recirculation is that the mixing of the gases permits better distribution of hydrogen when there is a great deal of nitrogen, and improves the operation with a hydrogen-nitrogen mixer, by avoiding a stratification phenomenon.

The practice of recirculation, however, suffers from drawbacks: one is that a recirculator is a complex rotary machine, subjected to delicate conditions of operation (the possible presence of water in liquid state resulting from condensation); another drawback is that a continuous circulation does not always permit eliminating completely water in

liquid phase from the cells, because the movement of the gas created is not always sufficiently abrupt.

The invention has for its object to create abrupt purges (which is to say with a relatively large and rapid pressure drop), whilst limiting to the extent possible the losses of purged gas from the circuit, for example the loss of hydrogen from the hydrogen circuit, and the loss of oxygen from the oxygen circuits.

To this end, the invention relates to a purge process for the gas circuit of a fuel cell, in which there is introduced at least one gas from a supply of gas to an input of the gas circuit of the cell and residual products are removed at an evacuation outlet or purge of the gas circuit of the cell, according to which process at least the water in liquid state located in the gas circuit, is evacuated at intervals that are regular or not, by the outlet; characterized in that the cell being connected to a storage by at least connection means connecting the outlet of the cell to an inlet of the storage, and the gas pressures in the respective reference regions of the cell and of the capacity being momentarily approximately equal, the pressure of the gas in the cell and in the storage is decreased, then there is established, from gas from the supply, a rapidly increasing gas flow passing through the connection means, of the battery to the storage, so as to transport simultaneously water in liquid phase contained in the battery, into the storage.

The process can moreover have one or several of the following characteristics:

- to approximately equalize the pressures in the cell and in the storage, the arrival of gas from the feed to the inlet of the cell is interrupted, then the pressure in the storage and in the cell is decreased, typically to about atmospheric pressure, by letting the cell consume gas from the cell and from the storage without resupplying the cell with gas, and the cell is resupplied to increase the pressure in it, and finally the cell and the storage are again placed in communication by opening the connection means;

The invention also relates to a device which comprises a fuel cell having at least two gas circuits of which at least one comprises a circuit gas inlet connected by an inlet circuit to a gas supply and an outlet for evacuating or purging the gas circuit, and a storage comprising an inlet connected to the outlet of the cell by connection means.

Other characteristics and advantages of the invention will become apparent from the following description, of embodiments of method and construction of the invention, given by way of non-limiting example, and illustrated by the accompanying drawings, in which:

- Figures 1 to 7 are block diagrams respectively of seven devices for practicing the process according to the invention, in which the same reference numerals indicate the corresponding elements from one figure to another, and

- Figure 8 is a curve representative of the voltage delivered by the fuel cell as a function of time elapsed from its being placed in service, respectively for a cell in which there is no purge, for a cell periodically purged according to the prior art, and for a cell periodically purged according to the invention.

The drawings show a fuel cell 1, comprising an inlet 11 for a gas circuit by which a gas permits operation of the cell, from a gas supply (not shown), which is introduced into the latter, and an outlet 12 for evacuation or purging of gas, by which a desired residual portion of gas which has not been used, as well as the liquid phase water which has passed through the membrane of the cell, are evacuated, this possible residual gas and this water constituting the obstacles to the free circulation of new gas. In the examples which follow, the gas circuit is a hydrogen circuit, and there can be, as residual gas, hydrogen, and as will be seen, nitrogen.

According to the invention, the outlet 12 of the cell 1 is connected to an inlet of a storage 2 whose volume is the order of that of the anode compartment of the cell, by connection means 3 comprising a conduit 30. At regular intervals, or not, the pressure in at least one reference region of the cell located between the inlet 11 and the outlet 12 is approximately equalized, as well as that of the storage, at a value P; then the gas pressure is decreased at least in the storage 2, then there is established, with gas from the feed, a rapidly increasing gas current, passing through the

connection means, from the cell to the storage, so as to convey simultaneously liquid phase water contained in the cell, to the storage; after this, the water in liquid phase is evacuated from the storage.

In many cases, it is practical that, the value P being greater than atmospheric pressure, the pressure value at which the gas flow is established will be approximately equal to atmospheric pressure.

The values which follow, given by way of example, correspond to a fuel cell of 30kW and whose internal volume is 24 liters.

In Figure 1, the connection means 3 comprise, in addition to the outlet conduit 30 from the cell, an outlet valve 31 interposed in this conduit, and yielding pressure drops as small as possible; in normal operation (between purges), this valve 31 can be open or closed; in the inlet circuit 4 of the cell 1 connecting the cell to a gas supply (not shown), a valve 41 is connected to the inlet 11 of the cell; in normal operation (between purges), this valve 41 is open. So as to proceed to purge, the outlet valve 31 is opened if it is initially closed, then successively:

- the arrival of gas from the supply is interrupted, at the inlet 11 of the cell, and to do this the inlet valve 41 is closed; following consumption of the gas present in the cell, which is not resupplied, the pressure which initially as P in the cell 1 and in the storage 2, decreased to $P-\Delta P$; in

the selected example, the pressure drop ΔP is of the order of 0.1 bar every two seconds;

- when ΔP reaches a predetermined value of the order of 0.1 bar to 0.6 bar, the storage is shut off from the cell, and to do this the outlet valve 31 is closed, and the cell is resupplied; and to do this, the inlet valve 41 is immediately opened, which gives rise to a pressure increase in the cell 1;

- finally, when the pressure in the cell 1 has returned to its initial value P, the cell and the storage are again placed in communication; and to do this, the outlet valve 31 is reopened, which gives rise to a rapidly increased gas current to the cell and, passing through the connection means 3, from the cell to the storage, carrying the liquid phase water contained in the cell, to the storage 2; it then suffices to purge the storage to evacuate the water, by means of a purge member 21 which can also be a valve.

In Figure 2, the connection means 3 comprise an outlet conduit 30 but no outlet valve, because the pressure drops of the inlet circuit 4 comprising the inlet valve 41 are supposedly sufficiently low so as not to impose any limitation on the gas flow. In this case, for purging, the arriving gas at the entry of the cell is interrupted; and to do this, the inlet valve 41 is closed, the pressure falls by ΔP in the cell 1 and in the storage 2, as in the case of Figure 1, and the cell is resupplied; and to do this, the inlet valve 41 is opened, which gives rise to a rapidly increasing gas flow toward the cell, into the cell, and from the cell to the

storage, carrying along the water contained in the cell. If the pressure drops in the inlet circuit 4 are too great, a buffer storage 42 can as a modification be disposed in this circuit, upstream of the inlet valve 41 (in broken lines in Figure 2), to store new gas in a predetermined quantity and at a predetermined pressure.

In the two examples which have been described, the frequency of the purges of the cell 1 is limited only by the rapidity of consumption of gas in the cell. Moreover, the turbulence created by the abrupt movements of the gas can improve the operation in the presence of nitrogen. However, if too great a quantity of nitrogen is present, it is necessary to carry out a purge of the excess nitrogen. The presence of an excess of nitrogen is detected by the observation of a decrease in performance of the cell at the time of pressure drop. In the first example, the presence of the storage 2 permits limiting the loss of hydrogen, because to purge nitrogen, the valve 31 separating the storage 2 and the cell 1 is closed, and the storage 2 is opened to the outside, which evacuates a portion of the mixture impoverished in hydrogen, which is located there (one-third for an operation at 1.5 bars); during return to the conditions of normal operation, the quantity of hydrogen in the anode portion is increased, and a portion of the mixture is replaced which is impoverished by the new hydrogen (1/6th in this case).

In Figure 3, the connection means 3 again comprise an outlet conduit 30 and an outlet valve 31 disposed in this

conduit; moreover, the storage 2 comprises an outlet 22 connected by a return circuit 5 to the cell 1, so as to re-inject thereinto the hydrogen contained in the storage, instead of evacuating from the storage by means of a purge member 21 which then serves solely to evacuate water and nitrogen; to this end, the return circuit 5 comprises a pump 50 interposed in a conduit 51 of the return circuit connecting the outlet of the storage in this case to the inlet circuit 4; a purge member 52 is also connected to the outlet of the pump 50.

The device shown in this Figure 3 permits carrying out abrupt and regular purges whilst returning the hydrogen to circulation because the pressure in the storage 2 is decreased by means of the pump 50 by which the hydrogen contained in the storage is re-injected, for example upstream of the cell 1 (immediately adjacent the inlet 2 or farther upstream), or even downstream of the cell but upstream of the outlet valve 31 (shown in broken line in Figure 3), the hydrogen being then reintroduced into the cell though the outlet 12 of the latter. With this device, the outlet valve 31 is closed, and the pressure in the storage is decreased to the value P-ΔP; when this value is reached, the outlet valve 31 is opened, and thus there is established a rapidly increasing gas current from the cell to the storage, carrying the water in liquid phase contained in the cell, into the storage, for its evacuation.

This device and this process permitting a recirculation of the hydrogen, require the use of a pump. However,

this solution has its advantage, relative to the prior art technique using a circulator, that the pump need not circulate large quantities of hydrogen under a low pressure ΔP, but simply need drop the pressure in the storage during the interval of time which separates two purges. In the same example as before (cell of 30kW and 24 liters), with a purge every two minutes for a pressure difference of 0.5 bar, the flow rate is 6 Nl/mn, and can thus be ensured by a miniature pump of several watts. But the fundamental advantage of this device and of this process is that the cell is no longer placed under vacuum in the course of a purge, and there is accordingly no drop in performance even the slightest, in the course of this under-pressuring, except when the storage receives nitrogen, which permits detecting the moment at which the storage must be purged.

The devices of Figures 1, 2 and 3 require purging the storage to eliminate nitrogen and various impurities; they can be provided, so as to re-inject into the cell only hydrogen and to purge the impurities with a minimum loss of this gas, with purification means for example of palladium, an organic membrane, or a molecular sieve.

In Figure 4, the connection means 3 comprise an outlet conduit 30 and an outlet valve 31 of the three-passage type. The storage 2 is provided with a separation apparatus 23, in this case a membrane, to recover the hydrogen present in the latter. The outlet of this apparatus 23 is connected by a return circuit 5 comprising a conduit 51 with a second

inlet (third passage) of the valve 31. The device also comprises an inlet valve 41 in its inlet circuit 4, and a purge member 21 for the storage, such as a valve. The process used in this device, which is an improvement on that of Figure 1, is the following: for purging, the inlet valve 41 is closed, and the inlet of the outlet valve 31 is placed in communication with the outlet 22 of the separation apparatus 23 such that the cell 1 draws in the content of the storage 2 through the membrane of the separation apparatus 23; when the pressure in the storage reaches the value P-ΔP or stabilizes at a higher value (which then signifies that there is almost no more nitrogen and impurities in the storage); then at this point the outlet valve 31 is closed and the inlet valve 41 is opened; after which the storage is purged if the pressure stabilizes at a value higher than P-ΔP (or at a predetermined value), to eliminate at least a portion of the impurities; thus there is reached a value P-ΔP (for example adjacent atmospheric pressure) in the storage; finally, the inlet of the outlet valve 31 is placed in communication with the inlet of the storage by the outlet conduit 30, and thus the cell is purged as was described for the device of Figure 1.

As modifications (not shown):

- there could be connected at the outlet for purging the storage, a suction pump for the impurities, permitting reaching a lower pressure in the storage and eliminating more impurities;

- the three-passage outlet valve 31 could be replaced by a conventional valve with two flaps, namely a return flap for hydrogen pumping (in a direction from the separation apparatus 23 toward the cell), and a purge flap (in a direction from the cell toward the storage).

In Figure 5, showing a device which is a development of that of Figure 2, in which the connection means comprise an outlet conduit 30 but no outlet valve; thus, the outlet valve is in this case replaced by a principal flap 32 whose passing direction is from the cell 1 toward the storage 2, and a return circuit 5 comprises a return flap 52 for pumping hydrogen which connects the separation apparatus 23 to upstream of the principal valve 32 with a passing direction from this apparatus 23 upstream. During intake, already described in relation to the device of Figure 4, the flap 52 for pumping hydrogen opens and permits the transfer of hydrogen from the storage to the cell, which decreases the pressure in the storage; when there is no more hydrogen in the storage, the pressure again falls in the cell, but cannot fall over in the storage; if the storage is purged, the principal flap 32 does not open to the extent the cell remains at a lower pressure than the storage; after this, the purge member 21 is re-closed, the inlet valve 41 is opened, and thus there is established a flow of purge gas as in the case of Figure 2.

With the devices of Figures 4 and 5, there can also be carried out the purge of the cell without closing the purge member of the storage, by selecting a geometry of the storage

which promotes the piston effect exerted by the gas leaving the cell; there is thus eliminated a larger part of the accumulated impurities.

In Figure 6, which shows a device which is a development of that of Figure 3, the connection means 3 also comprise an outlet conduit 30 and an outlet valve 31 disposed in this conduit; the storage 2 is provided with a hydrogen separation apparatus 23, with a membrane; it is this apparatus 23 which is connected by a return circuit 5 to the inlet 11 of the cell or to the inlet circuit 4, or else upstream of the outlet valve 31 (shown in broken line in Figure 6) so as to re-inject into the cell the hydrogen contained in the storage, the return circuit 5 comprising a pump 50 incorporated in the return conduit 51 as described in connection with Figure 3. As before, the hydrogen is thus drawn from the storage toward the pump this time by means of the selective membrane, and then transmitted from the pump to the cell; the purge procedure is with this difference almost the same as that which has been described with reference to Figure 3. As is the case for the devices of Figures 4 and 5, the requirement to purge the storage is detected when the pressure in the latter stabilizes above the usual pressure.

In Figure 7 is shown a device which is also a modification of the device of Figure 1; there is therefore again an outlet valve 31 between the cell and the storage, the purge member 21 for the storage, and an inlet valve 41, in the same mounting; simply said, the conventional inlet valve 41 is

replaced by a three-passage valve whose second inlet (third passage) is connected by a return circuit 5 comprising a conduit 51, to the outlet 22 of the storage.

As in the preceding cases, in which there is an outlet valve 31, the latter can be in normal operation open or closed; the inlet valve 41 connects the cell to the hydrogen supply; at an appropriate time, the position of the inlet valve is reversed and the pressure in the storage is decreased by transferring gas from the latter to the cell; then the outlet valve 31 is closed if it was open; when the pressure in the storage has decreased to the selected value, the position of the inlet valve 41 is reversed to return the cell into communication with the gas supply, and the outlet valve 31 is opened and thus there is established a rapidly increasing gas flow carrying the water from the cell to the storage, after which the outlet valve 31 is re-closed to isolate the cell from the storage, if such are the normal operating conditions.

The same type of modification can be carried out with respect to Figure 2, and thus, in an embodiment (not shown), Figure 2 is modified by replacing the conventional inlet valve 41 by a three-passage valve whose second inlet is connected by a return circuit to the outlet of the storage.

Naturally, the problem of the appearance of water is not limited to the hydrogen circuit of a fuel cell, but it also exists in the oxygen circuit.

The examples described above, which do not rely on techniques specific to hydrogen, namely those of Figures 1, 2,

3 and 7, are also applicable to the pure oxygen circuit of such hydrogen-oxygen cells. Moreover, the greater quantity of water present on the oxygen side requires more frequent purges, but the frequency depends, as for hydrogen, on the cell; on the other hand, there is less trouble from the accumulation of other gases.

It will be noted that the frequency of the purges of the storage (of water, of nitrogen, etc.) can be very much less than that of the purges of the cell.

The efficiency obtained by practice of the invention can be seen in Figure 8, which shows in several cases the voltage delivered by a fuel cell such as that described above by way of example, as a function of time: the curve A represents the voltage delivered by the cell as a function of time when this cell is not purged, the voltage whose rapidity of decrease is characteristic; curve B shows the voltage for an identical cell in which the hydrogen circuit is purged every five minutes, according to the prior art process, but losing hydrogen with each purge; curve C shows the voltage for an identical cell in which the hydrogen circuit is purged by means of the process of the device according to the invention shown in Figure 1. This latter curve shows perfectly the constancy of performance with time, of a cell thus purged according to the invention.

CLAIMS

1. Process for purging the gas circuit of a fuel cell in which gas from a gas supply is introduced into an inlet (11) of a gas circuit of the cell and residual products are evacuated at an evacuation or purge outlet (12) of the gas circuit of the cell, in which process there is evacuated, at intervals that are regular or not, through the outlet (12), at least liquid phase water in the gas circuit, characterized in that, the cell (1) being connected to a storage (2) by at least an action means (3) connecting the outlet (12) of the cell (1) to an inlet of the storage (2), and the gas pressures in the respective reference regions of the cell and of the storage being momentarily approximately equal, the gas pressure in the cell and in the storage is decreased, and then there is established, from supply gas, a rapidly increasing gas flow passing through the connection means (3), from the cell to the storage, so as to transport simultaneously liquid phase water contained in the cell, into the storage.

2. Process according to claim 1, characterized in that, to substantially equalize the pressures in the cell (1) and the storage (2), the arrival of gas from the supply to the inlet (11) of the cell is interrupted, the pressure in the

storage and in the cell is decreased by letting the cell consume gas from the cell and from the storage without resupplying the cell with gas, and the cell is resupplied to cause the pressure to rise at least in this latter.

3. Process according to claim 2, characterized in that, to establish a rapidly increasing gas flow, the storage is first of all temporarily isolated from the cell by closing the connection means (3).

4. Process according to claim 3, characterized in that, to resupply the cell (1), new gas is first stored upstream of the inlet (11) of the cell (1) whilst the arrival of gas at this inlet is interrupted.

5. Process according to claim 1, characterized in that, to decrease the gas pressure in the storage (2), the storage is isolated from the cell (1) by closing the connection means (3), and gas is pumped from the storage and transferred into the cell through a return circuit (5) which re-injects it upstream or downstream of the cell.

6. Process according to claim 1, characterized in that, during decrease of pressure in the storage (2) and the cell (1), a portion of the gas in the storage is caused to pass to the cell through a gas separation apparatus, and if the pressure in the storage does not fall to a predetermined value, the storage is purged, then the rapidly increasing gas current is established.

7. Process according to one of claims 1 to 6, characterized in that the gas pressure is decreased at least in the cell and the storage (2) to reach a predetermined value adjacent atmospheric pressure.

8. Device for practicing the process according to any one of claims 1 to 7, characterized in that it comprises a fuel cell (1) comprising at least two gas circuits of which at least one comprises a gas circuit inlet (11) connected by an inlet circuit (4) to a gas supply and an evacuation or purge outlet (4) for the gas circuit, and storage (2) comprising an inlet connected to the outlet (12) of the cell by connection means (3).

9. Device according to claim 8, characterized in that the inlet circuit (4) comprises an inlet valve (41) selectively to cause and interrupt the arrival of gas at the inlet of the cell.

10. Device according to claim 8, characterized in that the connection means (3) comprise an outlet valve (31) selectively to make communication between and to isolate the cell and the storage.

11. Device according to one of claims 8 to 10, characterized in that it comprises a return circuit (5) from an outlet (22) of the storage (2) to re-inject gas from the storage into a conduit adjacent the inlet or the outlet of the cell (1).

12. Device according to one of claims 8 to 11, characterized in that it comprises at least one three-passage valve (31, 41) whose inlet is connected to an outlet (22) of the storage by a return conduit (51).

13. Device according to claim 12, characterized in that it comprises at least one three-passage valve (31) of which one inlet is connected to an outlet (12) of the cell.

14. Device according to claim 12, characterized in that it comprises at least one three-passage valve (41) of which an outlet is connected to an inlet (11) of the cell.

15. Device according to one of claims 8 to 14, characterized in that the storage (2) comprises a gas separation apparatus (23).

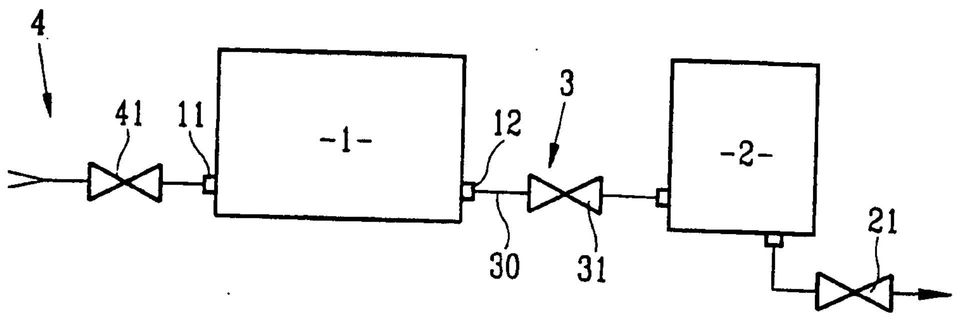


FIG.1

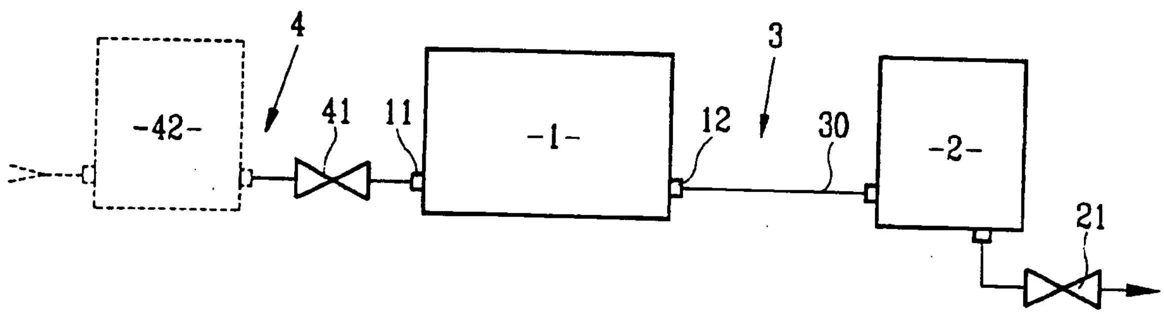


FIG.2

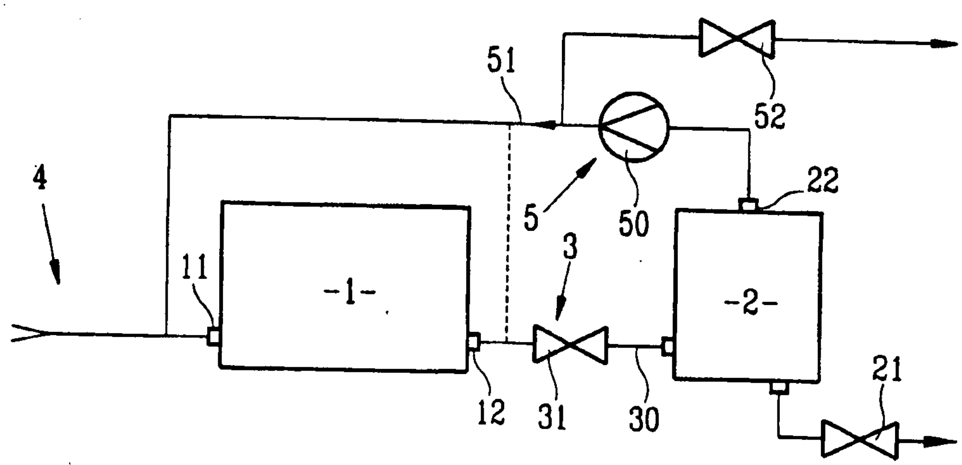


FIG.3

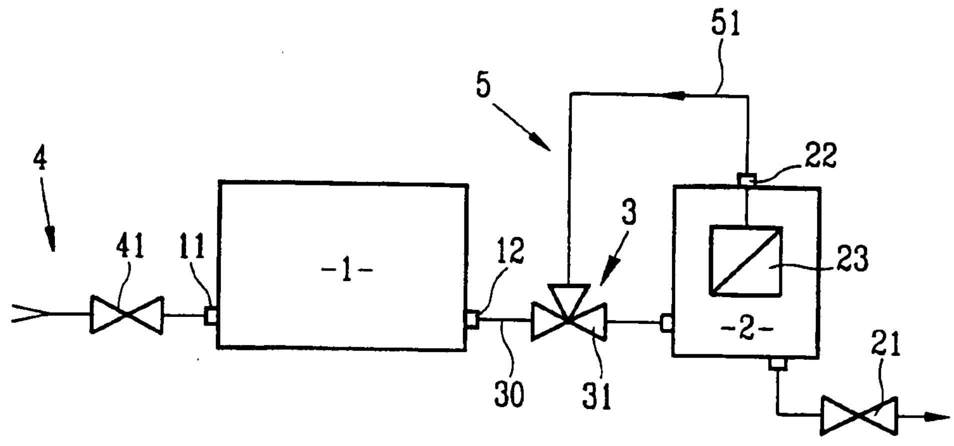


FIG.4

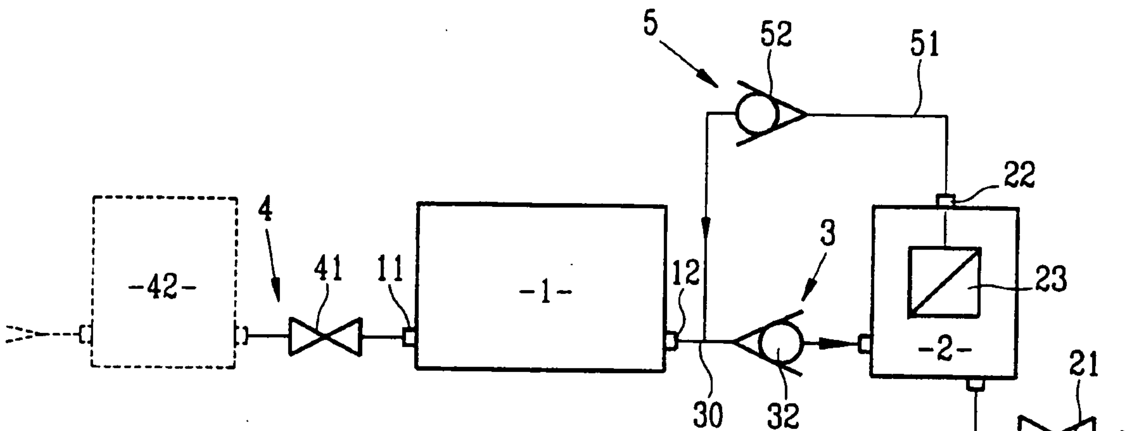


FIG.5

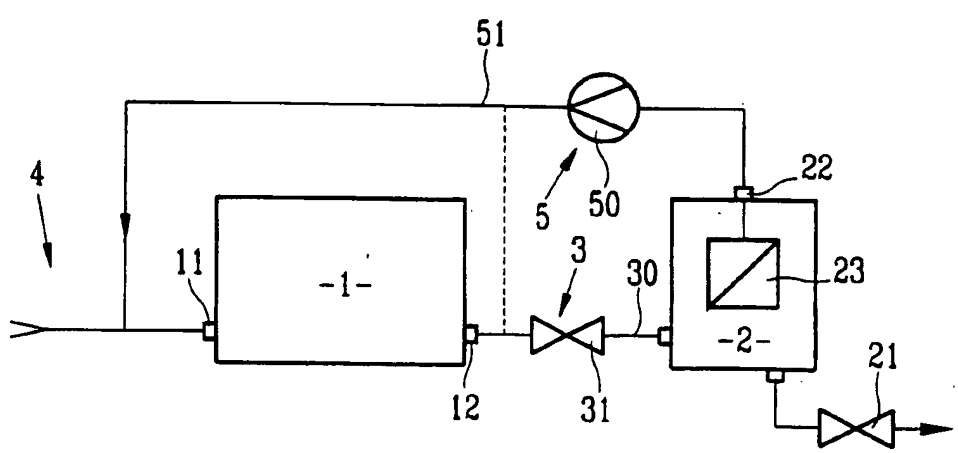
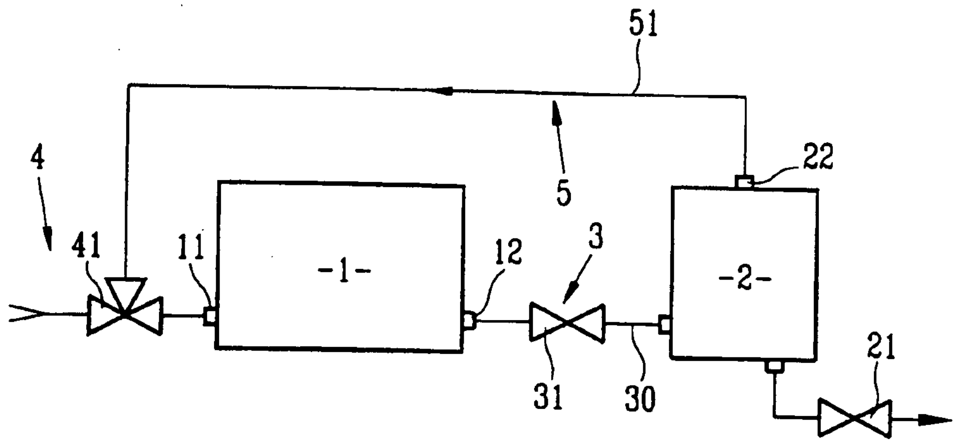


FIG.6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11
-1-
12
3
22
-2-
31
30
21

FIG.7

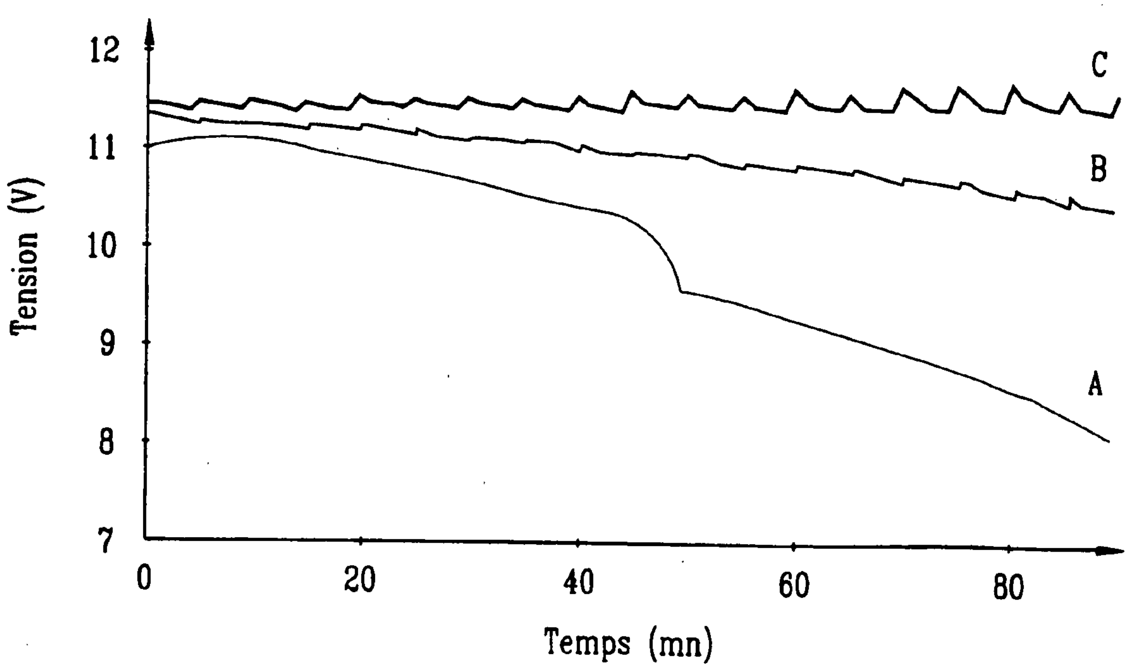
12
11
10
9
8
7
Tension (V)
C
B
A
0
20
40
60
80
Temps (mn)

FIG.8